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CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

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As the process of electrolysis is usually carried out there is very little opportunity to get any insight into its more minute mechanism. We are accustomed to think of each metal by having its own solution pressure, and by this we mean that it tends to go into solution under an impetus which varies with its position in the electro-motive force series. It is possible to calculate an osmotic pressure which would be just sufficient to balance this solution pressure and which would, if applied, cause equilibrium at the electrode. Under ordinary conditions electrochemical reactions are quite perfectly coupled. Equivalent amounts are dissolved at the anode and precipitated at the kathode, and it is not infrequent to state Faraday's Law in terms of the amounts thus dissolved and precipitated. But cases are well known where much more care must be taken in the statement of this law, as for example, where the air enters into reaction with one or both of the electrodes, or where the electrolyte itself attacks them. Very frequently a reaction of the form

$$M^{++} + M_{\text{metal}} \rightleftarrows 2\,M^{+}$$

causes a loss or gain not proportional to the amount of current which has passed through the electrolytic cell.

In the case of silver electrodes in a solution of silver nitrate it is usual to sum up the process as follows: —

During any unit of time after the circuit is closed

(1) An equivalent amount of silver dissolves at the anode.

(2) Silver migrates (as silver ion) toward the kathode and nitrate ion migrates toward the anode, each carrying its share of the current in proportion to its migration velocity.

(3) An equivalent amount of silver separates as metal at the kathode.

In the case of silver electrodes in pure water we might expect during each unit of time :

(1) At the anode, the formation of oxygen, or an oxide of silver, or the solution of silver, the sum total making one equivalent.

(2) The transfer of hydrogen ion (and later of silver ion if this is formed) toward the kathode, and of either or both of the ions O^{++} and OH^{-} toward the anode.

(3) At the kathode, evolution of hydrogen, and later precipitation of metallic silver, the two together making up one equivalent.

A case has recently come to my attention in which some of the more minute phenomena which accompany electrolysis are evident and in which lack of equivalence at the electrodes is especially evident. So far only qualitative observations have been made, but the data secured seem worthy of consideration.

FIGURE 1. Electrolysis on microscopic slide between silver electrodes.

If pure water be electrolysed between small silver electrodes at voltages ranging from 1.40 to about 3.8 volts, and the space between and about the electrodes be observed under the microscope with powers of 50 or so, the following series of minute phenomena are visible : —

(1) A very short time after the circuit is closed a cloud of brownish particles, very small and in violent Brownian movement, is formed in the neighborhood of the anode. If silver foil is used as anode it can be seen to dissolve rapidly and a dark film of silver oxide remains. The particles first make their appearance at a slight distance from the anode, and appear to be due to the formation of a silver compound produced from the silver which has dissolved and one of the constituents of the water.

(2) This cloud consists of approximately spherical particles of diameter 0.3 to 1.0 mikron. It is readily soluble in very dilute acetic acid and slightly soluble in water, forming an alkaline solution. The particles appear to be silver oxide.

(3) If a cell of form similar to that shown in Figure 1 is used for the electrolysis, the particles move along the floor of the cell toward the kathode. During their migration toward the kathode they follow the current lines, and Figure 2 shows drawings made about half a minute apart, indicating the general appearance under a low magnifying power. The masses which move in this way are not the single

particles, which would not be visible at this magnification, but are clumps each containing a great many individual grains.

(4) While the above is occurring in the neighborhood of the anode a thin cloud of totally different appearance *may* appear about the kathode. The particles of this cloud are metallic in appearance, and they later disappear suddenly and completely when the growth of metallic silver begins at the front of the kathode. The kathode cloud seems to be effected by external conditions in greater degree than that

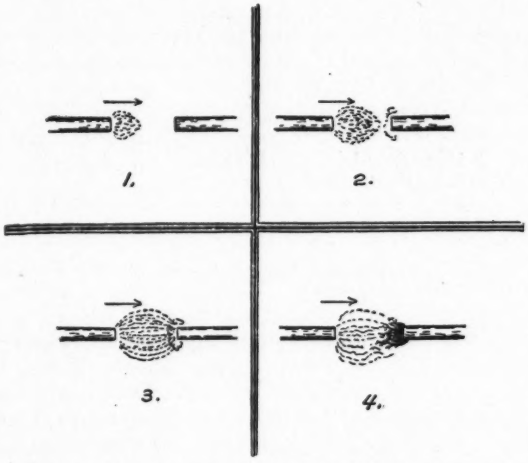

FIGURE 2. Minute phenomena of electrolysis between silver electrodes.

from the anode. It is a function of the separation of the electrodes and the character of the kathode surface.

(5) The above described effects appear in the purest obtainable water and they are most evident in the best conductivity water, which has been recently prepared in quartz vessels and kept carefully from contact with air.

Electrolytes in very small concentration prevent the effect completely and cause the appearance of the usual gas bubbles at the anode and kathode. The following brief table shows how a few electrolytes behave in this respect.

Sodium Hydroxide	0.015 *N*	Cloud.
	.020 *N*	very slight cloud and bubbles at anode.
	above .020 *N*	Only bubbles at anode.
Sodium Chloride	0.0005 *N*	brown cloud, soluble in drop of acetic acid.
	.001 *N*	brown, white } clouds brown soluble, white insoluble
	above .001 *N*	white cloud only.

(6) While the above effects are making their appearance in the electrolyte at slight distances from the electrodes nothing whatever happens at the kathode itself. The space between the electrodes may be active for several minutes without the appearance of either a bubble of gas or a crystal of silver. If very thin silver foil is used for electrodes solvent action on the anode is very evident and it is rapidly dissolved. A thin silver foil kathode shows signs of dissolving at the edges during the first minute or so of the passage of the current, but the action ceases immediately.

(7) There seems to be a limiting voltage below which these phenomena do not make their appearance. This is very close to 1.41 volts for electrodes 1 mm. apart. The upper limit of voltage, above which gas appears at the electrodes, is about 3.8 volts.

(8) Even in purest distilled water the phenomena are much more complicated than those so far described. The anode and kathode clouds are quite different in their behavior. That from the kathode appears to be composed of particles shot off at random, and these particles do not take any definite path after leaving the neighborhood of their parent electrode. The anode cloud, on the contrary, sticks closely together, and if the electrodes are at the mouth of a deep test-tube filled with water the anode cloud travels to the very bottom of the tube in such close coherence that it looks like a thin brown thread.

(9) The effect of a magnetic field on the behavior of these particles has been tried without definite result. They are relatively so large, and they move so slowly that an effect is hardly to be anticipated.

Attempt has been made to follow the changes in weight at each electrode during the electrolysis. The micro-balance was adapted for this purpose as shown in Figure 3. It is of course quite impossible to use any arrangement in which a fibre passes through the liquid surface. The effect of surface tension is far too great. But by placing both fibres and conducting wires under the surface of the electrolyte

the difficulty is easily overcome. The balance loses but a small percentage of its sensitiveness when used with a heavy metal like silver or copper.

The fibres used were of quartz and about 8 cm. long. The conducting wires were of platinum about 0.04 mm. in diameter, and these were welded to small pieces of silver wire and held fast in hooks at the end of the fibres, so that the silver electrodes were presented to each other at a distance of about 1.5 mm. The sensitiveness was such that a 0.1 mg. rider at the end of either fibre caused a deflection of more than a centimeter. One of the (large) divisions of the micrometer

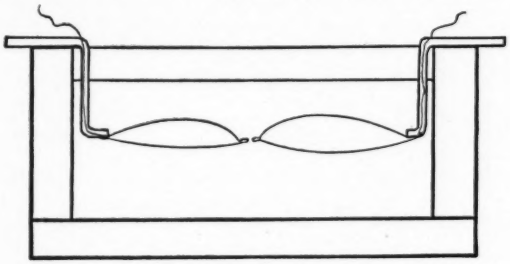

FIGURE 3. Microcoulometer.

eyepiece of the observing microscope corresponds to a change in weight of about 0.0001 mg., and a fraction of a division is easily read.

With this instrument the following qualitative changes were noticed.

(1) Immediately on closing the circuit a very slight *decrease* in the weight of each electrode. This change was observed in four of six experiments and must therefore be classed as doubtful until further proof is obtained of its correctness.

(2) Thereafter for several minutes an *increase* in the weight of each electrode, the anode gaining much faster than the kathode. This effect is quite certain and considerable. It is accompanied by a change in color at the anode, which turns dark, and probably represents the formation of silver oxide or peroxide. The increase in weight at the kathode is seen to be due to the deposition of silver.

(3) From then on decrease in weight at the anode, and increase at the kathode, finally approaching proportionality.

The most important point which has been brought out in this preliminary exploration seems to be that of the complete lack of equiva-

lence at the two electrodes. As observed under a high power, the entire anode may be eaten away, and the electrolyte space filled with masses of silver oxide, in some cases without a visible change at the kathode. Not even a bubble of gas makes its appearance. If platinum is used as kathode in place of silver, not the smallest amount of current can be sent through the cell without the appearance of streams of minute bubbles.

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